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(54) **(Co)polymerization process in aqueous emulsion of fluorinated olefinic monomers**

Verfahren zur (Co-)Polymerisation von fluorenthaltenden olefinischen Monomeren in wässriger Emulsion

Procédé de (co)polymérisation en émulsion aqueuse de monomères oléfiniques fluorés

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Description

[0001] The present invention relates to microemulsions of fluoropolyoxyalkylenes having hydrogenated end groups and/or hydrogenated repetitive units.

[0002] Said emulsions are useful in (co)polymerization processes in aqueous emulsion of fluorinated olefinic monomers.

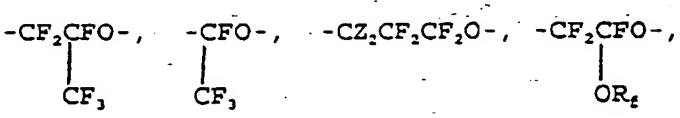
[0003] The Applicant has surprisingly found that an aqueous microemulsion of a fluoropolyoxyalkylene having hydrogenated end groups and/or hydrogenated repetitive units added to the reaction medium of a (co)polymerization process in aqueous emulsion of fluorinated olefinic monomers, affords a remarkable reduction in the induction period compared with the same process carried out in the presence of a microemulsion of perfluoropolyoxyalkylenes. By induction period it is meant the time running from the moment when the addition of the radical initiator begins to the moment when the actual starting of the (co)polymerization is observed, as pointed out by a monomer consumption.

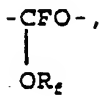
[0004] This fact constitutes a remarkable advantage both for the quality of the final product and for the industrial application of said process. In fact, a short induction period minimizes the formation of low molecular weights, which, as known, mainly occurs in the first phase of the reaction, and then leads to a narrower molecular weight distribution. As evidenced by the experiments carried out by the Applicant, the product obtained with the process object of the present invention is also characterized by a lower concentration of end groups deriving from the radical initiator and therefore by a higher thermal stability. Moreover, when operating with a discontinuous process, a lower induction period involves a reduction in the "cycle time", namely the time running from a productive cycle to the other, with evident advantages for a production on an industrial scale.

[0005] It is therefore object of the present invention a microemulsion of the oil-in-water or water-in-oil type, macroscopically formed by a sole liquid phase having a limpid or opalescent appearance, stable in a certain temperature range, comprising:

(a) an aqueous solution;

(b) a fluoropolyoxyalkylene constituted by repetitive units, randomly distributed along the chain, selected from: -CFZO-, $-CF_2CFZO-$,





where Z is H or F, R_f is $-CF_3$, $-C_2F_5$, or $-C_3F_7$; and by hydrogenated end groups selected from $-CF_2H$, $-CF_2CF_2H$, $-CFH-CF_3$, and $-CFH-OR_f$, where R_f is defined as above, or perfluorinated end groups selected from $-CF_3$, $-C_2F_5$ and $-C_3F_7$, at least one of the end groups being hydrogenated;

(c) a fluorinated surfactant selected from the following classes: perfluorocarboxylic or perfluorosulphonic acids C_5-C_{11} and salts thereof; mono- or bi-carboxylic acids deriving from perfluoropolyoxyalkylenes and salts thereof; non-ionic surfactants formed by a perfluoropolyoxyalkylene chain bound to a polyoxyalkylene chain; cationic surfactants having one or more perfluoroalkyl and/or perfluoropolyoxyalkylene chains.

[0006] The average molecular weight is generally comprised between 300 and 4000, preferably between 400 and 1500.

[0007] In particular, such fluoropolyoxyalkylenes can be selected from the following classes:

(a)

$$T_1\text{-}O(CF_2\text{-}\underset{\displaystyle CF_3}{\underset{|}{C}}FO)_a(CFXO)_b\text{-}T_2$$

where:
T_1 and T_2, equal or different from each other, are hydrogenated groups $-CF_2H$, $-CFH-CF_3$, or perfluorinated groups $-CF_3$, $-C_2F_5$, $-C_3F_7$, at least one of the end groups being hydrogenated; X is -F or $-CF_3$; a, b are numbers such that the molecular weight is comprised in the range indicated above, a/b is comprised between 5 and 15;
(b)

$$T_3\text{-}O(CF_2CF_2O)_c(CF_2O)_d\text{-}T_4$$

where:
T_3 and T_4, equal or different from each other, are hydrogenated groups $-CF_2H$ or $-CF_2\text{-}CF_2H$, or perfluorinated groups $-CF_3$, $-C_2F_5$, at least one of the end groups being hydrogenated; c, d are numbers such that the molecular weight is comprised in the range indicated above, c/d is comprised between 0.3 and 5;
(c)

$$T_5\text{-}O(CF_2\text{-}\underset{\displaystyle CF_3}{\underset{|}{C}}FO)_e(CF_2CF_2O)_f(CFXO)_g\text{-}T_6$$

where:
T_5 and T_6, equal or different from each other, are hydrogenated groups $-CF_2H$, $-CF_2CF_2H$, or $-CFH-CF_3$, or perfluorinated groups $-CF_3$, $-C_2F_5$, $-C_3F_7$, at least one of the end groups being hydrogenated; X is -F or $-CF_3$; e, f, g are numbers such that the molecular weight is comprised in the range indicated above, e/(f+g) is comprised between 1 and 10, f/g is comprised between 1 and 10;
(d)

$$T_7\text{-}O(CF_2\text{-}\underset{\displaystyle CF_3}{\underset{|}{C}}FO)_h\text{-}T_8$$

where:
T_7 and T_8 are hydrogenated groups $-CFH-CF_3$, or perfluorinated groups $-C_2F_5$, $-C_3F_7$, at least one of the end groups being hydrogenated; h is a number such that the molecular weight is comprised in the range indicated above;
(e)

$$T_9\text{-}O(CZ_2CF_2CF_2O)_i\text{-}T_{10}$$

where:
Z is F or H; T_9 and T_{10}, equal or different from each other, are hydrogenated groups $-CF_2H$ or $-CF_2CF_2H$, or perfluorinated groups $-CF_3$, $-C_2F_5$, $-C_3F_7$, at least one of the end groups being hydrogenated; i is a number such that the molecular weight is comprised in the range indicated above;
(f)

$$T_{11}-O(CF_2O)_j(CF_2CFO)_k(CFO)_l-T_{12}$$
$$\qquad\qquad\qquad\qquad\quad |\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\quad OR_f\quad OR_f$$

where:
R_f is $-CF_3$, $-C_2F_5$, or $-C_3F_7$; T_{11} and T_{12}, equal or different from each other, are hydrogenated groups - CF_2H, $-CF_2CF_2H$, $-CFH-OR_f$, or perfluorinated groups-CF_3, $-C_2F_5$, $-C_3F_7$, at least one of the end groups being hydrogenated; j, k, l are numbers such that the molecular weight is comprised in the range indicated above, k+l and j+k+l are at least equal to 2, k/(j+l) is comprised between 10^{-2} and 10^3, l/j is comprised between 10^{-2} and 10^2;
(g)

$$T_{13}-O(CF_2-CFO)_m(CFXO)_n(CFHO)_o(CF_2CFHO)_p-T_{14}$$
$$\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\quad CF_3$$

where:
T_{13} and T_{14}, equal or different from each other, are hydrogenated groups $-CF_2H$, $-CFH-CF_3$, or perfluorinated groups $-CF_3$, $-C_2F_5$, $-C_3F_7$, at least one of the end groups being hydrogenated; X is -F or $-CF_3$; m, n, o, p are numbers such that the molecular weight is comprised in the range indicated above, m/n is comprised between 5 and 40, m/(o+p) is comprised between 2 and 50, o+p is at least 3, o is lower than p;
(h)

$$T_{15}-O(CF_2CF_2O)_q(CF_2O)_r(CFHO)_s(CF_2CFHO)_t-T_{16}$$

where:
T_{15} and T_{16}, equal or different from each other, are hydrogenated groups $-CF_2H$, $-CF_2-CF_2H$, or perfluorinated groups $-CF_3$, $-C_2F_5$, at least one of the end groups being hydrogenated; q, r, s, t are numbers such that the molecular weight is comprised in the range indicated above, q/r is comprised between 0.5 and 2, (q+r)/(s+t) is comprised between 3 and 40, s+t is at least 3, s is lower than t;
(i)

$$T_{17}-O(CF_2-CFO)_u(CF_2CF_2O)_v(CFXO)_w(CFHO)_x(CF_2CFHO)_y-T_{18}$$
$$\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\quad CF_3$$

where:
T_{17} and T_{18}, equal or different from each other, are hydrogenated groups $-CF_2H$, $-CF_2CF_2H$, $-CFH-CF_3$, or perfluorinated groups $-CF_3$, $-C_2F_5$, $-C_3F_7$, at least one of the end groups being hydrogenated: X is -F or $-CF_3$; u, v, w, x, y are numbers such that the molecular weight is comprised in the range indicated above, (u+v)/w is comprised between 5 and 40, (u+v)/(x+y) is comprised between 2 and 50, x+y is at least 3, x is lower than y.

[0008] They are products obtainable by hydrolysis and subsequent decarboxylation of the -COF groups present in the corresponding perfluoropolyoxyalkylenes, as described for instance in the patents EP-A-154,297, US-A-4,451,646 and US-A-5,091,589.

[0009] The starting perfluoropolyethers containing the -COF groups as end groups and/or along the chain are described, for instance, in the patents GB-A-1,104,482 (class (a)), US-A-3,715,378 (class (b)), US-A-3,242,218 (class (c)), US-A-3,242,218 (class (d)), EP-A-148,482 (class (e)), EP-A-445,738 (class (f)), EP-A-244,839 and EP-A-337,346 (classes (g), (h), (i)).

[0010] The microemulsions of the invention can also contain co-surfactants, such as low chain (C_1-C_6) hydrogenated or fluorinated alcohols. Salts soluble in water can also be added, in order to increase the ionic strength of the aqueous

phase and to modify the interface tension between the immiscible liquids.

[0011] The preparation of the microemulsions is performed by simply mixing the components, without the need of supplying the system with a remarkable dispersion energy, as it occurs, on the contrary, in the case of conventional emulsions.

[0012] According to the experiments carried out by the Applicant, the replacement of a perfluoropolyoxyalkylene with a fluoropolyoxyalkylene having hydrogenated end groups and/or hydrogenated repetitive units as oil phase does not involve substantial modifications of the criteria reported in the patent US-A-4,990,283 that describes microemulsions of perfluoropolyoxyalkylenes, to lead the skilled person in the formulation of the microemulsions. Of course, under the same conditions, the presence of hydrogenated end groups and/or hydrogenated repetitive units involves a different affinity with respect to the other components, whereby it is often necessary to slightly modify the concentration of the components with respect to the corresponding perfluoropolyoxyalkylene microemulsions. However, for the skilled person it is sufficient to carry out some tests in order to find the proper combination of parameters which allow to obtain the desired microemulsion.

[0013] (Co)polymerization reactions wherein the microemulsions of the invention can be used occur, as known in the art, in the presence of suitable initiators, such as inorganic peroxides (for instance, ammonium or alkali metal persulphates) or organic peroxides (for instance, disuccinylperoxide, terbutyl-hydroperoxide, diterbutylperoxide), or also azocompounds (see US-A-2,515,628 and US-A-2,520,338). It is also possible to employ organic or inorganic redox systems, such as ammonium persulphate/sodium sulphite, hydrogen peroxide/aminoimimomethansulphinic acid.

[0014] The amount of radical initiator is that usually employed for the (co)polymerization of fluorinated olefinic monomers, and it is generally comprised between 0.003% and 5% by weight with respect to the total amount of (co)polymerized monomers.

[0015] It is important to point out that the use of fluoropolyoxyalkylenes having hydrogenated end groups and/or hydrogenated repetitive units instead of the corresponding perfluoropolyoxyalkylenes allows a greater flexibility in the selection of the initiator, since the presence of hydrogenated end groups increases the affinity with non-fluorinated products. It is thus possible to employ hydrogenated organic peroxides insoluble in water and in perfluoropolyoxyalkylenes, such as for example bis-(4-t-butylcyclohexyl) peroxydicarbonate.

[0016] As known, the emulsion technique requires also the presence of surfactants to stabilize the polymer particles in the latex. Since the surfactants used in the fluoropolyoxyalkylenes microemulsion are of the same kind of those commonly used in this kind of (co)polymerizations, generally it is not necessary to add other surfactants, the amount present in the microemulsion being per se sufficient to the purpose. If this situation does not occur, it is always possible to add other surfactants, which can be selected from the products having the formula:

$$R_f\text{-}X^- M^+$$

where R_f is a (per)fluoroalkyl chain C_5-C_{16} or a (per)fluoropolyoxyalkylene chain, X^- is $-COO^-$ or $-SO_3^-$, M^+ is selected from: H^+, NH_4^+, alkali metal ion. Among those most commonly used we cite: ammonium perfluoro-octanoate, (per) fluoropolyoxyalkylenes terminated with one or more carboxylic groups.

[0017] The reaction temperature can vary within a wide range, generally comprised between 10° and 150°C, preferably between 50° and 80°C, while the pressure is generally comprised between 1 and 10 MPa, preferably between 1.5 and 4 MPa.

[0018] In the process wherein the microemulsions of the present invention can be used, can be employed all kinds of fluorinated olefinic monomers, optionally containing hydrogen and/or chlorine and/or bromine and/or iodine and/or oxygen, provided that they are able to give (co)polymers by reaction with radical initiators in aqueous emulsion. Among them we can cite: perfluoroolefins C_2-C_8, such as tetrafluoroethylene (TFE), hexafluoropropene (HFP), hexafluoroisobutene; hydrogenated fluoroolefins C_2-C_8, such as vinylfluoride (VF), vinylidene fluoride (VDF), trifluoroethylene, perfluoroalkylethylenes CH_2=CH-R_f, where R_f is a perfluoroalkyl C_1-C_6; chloro- and/or bromo- and/or iodo-fluoroolefins C_2-C_8, such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene; (per)fluorovinylethers CF_2=CFOX, where X is a (per)fluoroalkyl C_1-C_6, for instance trifluoromethyl, pentafluoropropyl, bromodifluoromethyl, or a perfluorooxyalkyl C_1-C_9 having one or more ether groups, for instance perfluoro-2-propoxypropyl; perfluorodioxols.

[0019] The fluoroolefins can also be copolymerized with non-fluorinated olefins C_2-C_8, such as ethylene, propylene, isobutylene.

[0020] Some working examples are hereinunder reported, whose aim is merely illustrative but not limitative of the scope of the invention itself.

EXAMPLE 1

Preparation of the fluoropolyoxyalkylene microemulsion having hydrogenated end groups.

[0021] In a glass flask equipped with a stirrer, 26.1 g of demineralized H_2O, 20.0 g of a surfactant of the formula:

$$CF_3O(CF_2CF(CF_3)O)_m(CF_2O)_nCF_2COO^- K^+$$

having a m/n ratio = 26.2 and an average molecular weight of about 580, and 14.5 g of a fluoropolyoxyalkylene having the formula:

$$CF_2H\text{-}O(CF_2CF_2O)_m(CF_2O)_n\text{-}CF_2H$$

having a m/n ratio = 0.95 and an average molecular weight of 365, were added. At a temperature comprised between 14.7 and 39°C the mixture is the form of microemulsion, and it appears as a limpid, thermodynamically stable solution.

Copolymerization of tetrafluoroethylene and ethylene

[0022] A 5 l AISI 316 steel chromium-plated autoclave, equipped with a stirrer working at 570 rpm, was evacuated and 3.5 l of demineralized H_2O; 60.6 g of the fluoropolyoxyalkylene microemulsion having hydrogenated end groups previously prepared, corresponding to 20.0 g of surfactant, were added in sequence.

[0023] The autoclave was then brought to the reaction temperature of 60°C and loaded with an ethylene/TFE gaseous mixture in such an amount to obtain, at the working pressure of 22 absolute bar, an ethylene/TFE ratio in the gas phase of about 20/80 by mols. The pressure was maintained constant during the reaction by feeding an ethylene/TFE mixture with a ratio 49/51 by mols. When the working pressure was reached, ammonium persulphate (APS), in the form of an aqueous solution, was fed continuously for 2 hours with a flow rate of $3 \cdot 10^{-3}$ g/l·min

[0024] Taking as reference the moment in which the introduction of the initiator began, the reaction started after 10 minutes; after 195 minutes the reaction was stopped by cooling the autoclave at room temperature. The so obtained latex was then discharged, coagulated by mechanical stirring, washed with H_2O and dried. 928 g of a copolymer ethylene/TFE were obtained. The values of productivity (R_p) are reported in Table 1, expressed as grams of produced polymer per minute per H_2O liter.

EXAMPLE 2 (comparative)

Preparation of the perfluoropolyoxyalkylene microemulsion.

[0025] In a glass flask equipped with a stirrer, 20.0 g of the surfactant of the formula:

$$CF_3O\text{-}(CF_2\text{-}CF(CF_3)O)_n(CF_2O)_m\text{-}CF_2COO^- K^+$$

having n/m = 10 and average molecular weight of 580, 18.0 g of demineralized water and 12.0 g of Galden(R) DO2, of the formula:

$$CF_3O\text{-}(CF_2\text{-}CF(CF_3)O)_n(CF_2O)_m\text{-}CF_3$$

having n/m=20 and average molecular weight of 450, were mixed. At a temperature comprised between 0° and 55°C the mixture is in the form of a microemulsion and appears as a limpid solution.

Copolymerization of tetrafluoroethylene and ethylene.

[0026] Example 1 was repeated in the same conditions, using an amount of the perfluoropolyoxyalkylene microemulsion previously prepared such as to obtain 20.0 g of surfactant. By taking as zero time the time when the addition of the initiator began, the reaction started after 52 minutes; after 233 minutes the reaction was stopped and 934 g of a copolymer ethylene/TFE were obtained. The measured values of productivity (R_p) are reported in Table 1.

EXAMPLE 3

[0027] A 5 l AISI 316 steel chromium-plated autoclave, equipped with a stirrer working at 570 rpm, was evacuated, and 3.4 l of demineralized H_2O; 60.6 g of the fluoropolyoxyalkylene microemulsion having hydrogenated end groups of Example 1, corresponding to 20.0 g of surfactant; 64 g of terbutanol; 3 g of n-pentane as chain transfer agent, were introduced in sequence.

[0028] The autoclave was then brought to the reaction temperature of 60°C and charged with an ethylene/TFE gaseous mixture in such an amount to obtain, at the working pressure of 22 absolute bar, an ethylene/TFE ratio in the gas phase of about 20/80 by mols. The pressure was kept constant during the raction by feeding an ethylene/TFE mixture in a molar ratio 49/51. When the working pressure was reached, ammonium persulphate (APS), in the form of aqueous solution, was continuously fed for 2 hours with a flow rate of $3 \cdot 10^{-3}$ g/l·min. Taking as zero time the time when the addition of the initiator began, the reaction started after 26 minutes; after 223 minutes the reaction was stopped by cooling the autoclave at room temperature. The so obtained latex was discharged, coagulated by mechanical stirring, washed with H_2O and dried. 310 g of an ethylene/TFE copolymer was obtained. The values of the Melt Flow Index (MFI) (according to ASTM Method D 3159-83) and of the radical concentration, expressed as grams of $SO_4^{\cdot-}$ radicals produced during the reaction per polymer gram, are reported in Table 2.

[0029] From the so obtained copolymer a film having a thickness of 0.4 mm was molded, which was then submitted to ageing in air at 235°C for 144, 264 and 360 hours. The sample was analyzed at FT-IR in the absorption range corresponding to the double bonds (1800-1650 cm^{-1}), which form as a consequence of the degradation of the product. The values of the area of the absorption band in said range (A_t) are reported, measured at the different times of ageing, to which the area of the band at zero time (A_0) was subtracted.

EXAMPLE 4 (comparative)

[0030] Example 3 was repeated in the same conditions, using an amount of the perfluoropolyoxyalkylene microemulsion of Example 2 such as to obtain 20.0 g of surfactant. By taking as zero time the moment when the addition of the initiator began, the reaction started after 42 minutes; after 266 minutes the reaction was stopped and 310 g of an ethylene/TFE copolymer were obtained. The values of the MFI and of the radical concentration, measured as described in Example 3, are reported in Table 2.

[0031] From the so obtained copolymer a film having a thickness of 0.4 mm was molded, whose thermal stability was tested according to the method described in Example 3. The so obtained data are reported in Table 2.

TABLE 1

EX.	INDUCTION PERIOD (min)	REACTION TIME (min)	OBTAINED POLYMER (g)	R_p (g/l_{H2O}/min)	RADICAL CONC. (rad.g./pol.g.)
1	10	195	928	1.36	$4.81 \cdot 10^{-5}$
2(*)	52	233	934	1.14	$6.09 \cdot 10^{-5}$

(*) comparative

TABLE 2

EX.	MFI (g/10')	RADICAL CONC. (rad.g./pol.g.)	AGEING AT 235°C (A_t-A_0) (optical density units·cm^{-1})		
			144 h	264 h	360 h
3	4.1	$1.73 \cdot 10^{-4}$	2.6	4.3	5.7
4(*)	6.9	$2.18 \cdot 10^{-4}$	3.0	5.4	6.4

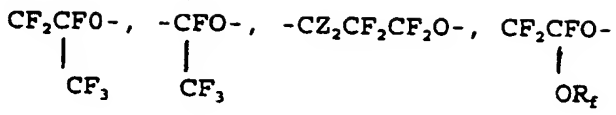
(*) comparative

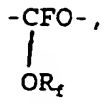
Claims

1. Microemulsion of the oil-in-water or water-in-oil type, macroscopically formed by a sole liquid phase having a limpid or opalescent appearance, stable in a certain temperature range, comprising:

   (a) an aqueous solution;
   (b) a fluoropolyoxyalkylene constituted by repetitive units, randomly distributed along the chain, selected from:

-CFZO, -CF_2CFZO-,





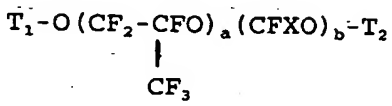
where Z is H or F, R_f is-CF_3, -C_2F_5, or -C_3F_7; and by hydrogenated end groups selected from -CF_2H, -CF_2CF_2H, -CFH-CF_3, and -CFH-OR_f, where R_f is defined as above, or perfluorinated end groups selected from -CF_3, -C_2F_5 and -C_3F_7, at least one of the end groups being hydrogenated;
(c) a fluorinated surfactant selected from the following classes: perfluorocarboxylic or perfluorosulphonic acids C_5-C_{11} and salts thereof; mono-or bi-carboxylic acids deriving from perfluoropolyoxyalkylenes and salts thereof; non-ionic surfactants formed by a perfluoro-polyoxyalkylene chain bound to a polyoxyalkylene chain, cationic surfactants having one or more perfluoroalkyl and/or perfluoropolyoxyalkylene chains.

2. Microemulsion according to claim 1, wherein the average molecular weight of the fluoropolyoxyalkylenes is comprised between 300 and 4000.

3. Microemulsion according to claim 1, wherein the average molecular weight of the fluoropolyoxyalkylenes is comprised between 400 and 1500.

4. Microemulsion according to anyone of claims from 2 to 3, wherein the fluoropolyoxyalkylenes are selected from the following classes:

(a)



where:
T_1 and T_2, equal or different from each other, are hydrogenated groups -CF_2H, -CFH-CF_3, or perfluorinated groups -CF_3, -C_2F_5, -C_3F_7, at least one of the end groups being hydrogenated; X is -F or -CF_3; a, b are numbers such that the molecular weight is comprised in the range indicated above, a/b is comprised between 5 and 15;
(b)

$$T_3\text{-}O(CF_2CF_2O)_c(CF_2O)_d\text{-}T_4$$

where:
T_3 and T_4, equal or different from each other, are hydrogenated groups -CF_2H or -CF_2-CF_2H, or perfluorinated groups -CF_3, -C_2F_5, at least one of the end groups being hydrogenated; c, d are numbers such that the molecular weight is comprised in the range indicated above, c/d is comprised between 0.3 and 5;
(c)

$$T_5\text{-}O(CF_2\text{-}\underset{\displaystyle CF_3}{\underset{|}{CFO}})_e(CF_2CF_2O)_f(CFXO)_g\text{-}T_6$$

where:
T_5 and T_6, equal or different from each other, are hydrogenated groups $-CF_2H$, $-CF_2CF_2H$, or $-CFH-CF_3$, or perfluorinated groups $-CF_3$, $-C_2F_5$, $-C_3F_7$, at least one of the end groups being hydrogenated; X is -F or $-CF_3$; e, f, g are numbers such that the molecular weight is comprised in the range indicated above, e/(f+g) is comprised between 1 and 10, f/g is comprised between 1 and 10;
(d)

$$T_7\text{-}O(CF_2\text{-}\underset{\displaystyle CF_3}{\underset{|}{CFO}})_h\text{-}T_8$$

where:
T_7, and T_8, are hydrogenated groups $-CFH-CF_3$, or perfluorinated groups $-C_2F_5$, $-C_3F_7$, at least one of the end groups being hydrogenated; h is a number such that the molecular weight is comprised in the range indicated above;
(e)

$$T_9\text{-}O(CZ_2CF_2CF_2O)_i\text{-}T_{10}$$

where:
Z is F or H; T_9 and T_{10}, equal or different from each other, are hydrogenated groups $-CF_2H$ or $-CF_2\text{-}CF_2H$, or perfluorinated groups $-CF_3$, $-C_3F_7$, $-C_3F_7$, at least one of the end groups being hydrogenated; i is a number such that the molecular weight is comprised in the range indicated above;
(f)

$$T_{11}\text{-}O(CF_2O)_j(\underset{\displaystyle OR_f}{\underset{|}{CF_2CFO}})_k(\underset{\displaystyle OR_f}{\underset{|}{CFO}})_l\text{-}T_{12}$$

where:
R_f is $-CF_3$, $-C_2F_5$, or $-C_3F_7$; T_{11} and T_{12}, equal or different from each other, are hydrogenated groups $-CF_2H$, $-CF_2CF_2H$, $-CFH-OR_f$, or perfluorinated groups $-CF_3$, $-C_2F_5$, $-C_3F_7$, at least one of the end groups being hydrogenated; j, k, l are numbers such that the molecular weight is comprised in the range indicated above, k+l and j+k+1 are at least equal to 2, k/(j+l) is comprised between 10^{-2} and 10^3, l/j is comprised between 10^{-2} and 10^2;
(g)

$$T_{13}\text{-}O(\underset{\displaystyle CF_3}{\underset{|}{CF_2\text{-}CFO}})_m(CFXO)_n(CFHO)_o(CF_2CFHO)_p\text{-}T_{14}$$

where:
T_{13} and T_{14}, equal or different from each other, are hydrogenated groups $-CF_2H$, $-CFH-CF_3$, or perfluorinated groups $-CF_3$, $-C_2F_5$, $-C_3F_7$, at least one of the end groups being hydrogenated; X is -F or $-CF_3$; m, n, o, p are numbers such that the molecular weight is comprised in the range indicated above, m/n is comprised between

5 and 40, m/(o+p) is comprised between 2 and 50, o+p is at least 3, o is lower than p;
(h)

$$T_{15}\text{-}O(CF_2CF_2O)_q(CF_2O)_r(CFHO)_s(CF_2CFHO)_t\text{-}T_{16}$$

where:
T_{15} and T_{16}, equal or different from each other, are hydrogenated groups $-CF_2H$, $-CF_2\text{-}CF_2H$, or perfluorinated groups $-CF_3$, $-C_2F_5$, at least one of the end groups being hydrogenated; q, r, s, t are numbers such that the molecular weight is comprised in the range indicated above, q/r is comprised between 0.5 and 2, (q+r)/(s+t) is comprised between 3 and 40, s+t is at least 3, s is lower than t;
(i)

$$T_{17}\text{-}O(CF_2\text{-}\underset{\displaystyle CF_3}{\underset{|}{CFO}})_u(CF_2CF_2O)_v(CFXO)_w(CFHO)_x(CF_2CFHO)_y\text{-}T_{18}$$

where:
T_{17} and T_{18}, equal or different from each other, are hydrogenated groups $-CF_2H$, $-CF_2CF_2H$, $-CFH\text{-}CF_3$, or perfluorinated groups $-CF_3$, $-C_2F_5$, $-C_3F_7$, at least one of the end groups being hydrogenated; X is -F or $-CF_3$; u, v, w, x, y are numbers such that the molecular weight is comprised in the range indicated above, (u+v)/w is comprised between 5 and 40, (u+v)/(x+y) is comprised between 2 and 50, x+y is at least 3, x is lower than y.

5. Microemulsion according to any of the preceding claims further comprising a co-surfctant.

6. Microemulsion according to claim 5 wherein the co-surfactant is selected from C_1-C_6 hydrogenated or fluorinated alcohols.

Patentansprüche

1. Mikroemulsion des Öl-in-Wasser- oder Wasser-in-Öl-Typs, die makroskopisch aus einer einzigen flüssigen Phase mit klarem oder opaleszierendem Aussehen gebildet ist, in einem bestimmten Temperaturbereich stabil ist, umfassend:

(a) eine wäßrige Lösung,
(b) ein Fluorpolyoxyalkylen aus repetitiven Einheiten, die willkürlich entlang der Kette verteilt sind, ausgewählt aus:
-CFZO, $-CF_2CFZO$-,

$$-\underset{\displaystyle CF_3}{\underset{|}{CF_2CFO}}-,\quad -\underset{\displaystyle CF_3}{\underset{|}{CFO}}-,\quad -CZ_2CF_2CF_2O-,\quad -\underset{\displaystyle OR_f}{\underset{|}{CF_2CFO}}-$$

$$-\underset{\displaystyle OR_f}{\underset{|}{CFO}}-,$$

worin Z H oder F bedeutet, R_f $-CF_3$, $-C_2F_5$ oder $-C_3F_7$ bedeutet, und aus hydrierten Endgruppen, ausgewählt aus $-CF_2H$, $-CF_2CF_2H$, $-CFH\text{-}CF_3$ und $-CFH\text{-}OR_f$, worin R_f wie vorstehend definiert ist, oder perfluorierten Endgruppen, ausgewählt aus $-CF_3$, $-C_2F_5$ und $-C_3F_7$, wobei mindestens eine der Endgruppen hydriert ist.

(c) ein fluoriertes grenzflächenaktives Mittel, ausgewählt aus folgenden Klassen: C_5-C_{11}-Perfluorcarbonoder -Perfluorsulfonsäuren und Salze davon, mono- oder bicarbocyclische Säuren, abgeleitet von Perfluorpolyoxyalkylenen, und Salze davon, nichtionische grenzflächenaktive Mittel, gebildet durch eine Perfluorpolyoxyalkylenkette, die an eine Polyoxyalkylenkette gebunden ist, kationische grenzflächenaktive Mittel mit einer oder mehreren Perfluoralkyl- und/oder Perfluorpolyoxyalkylenkette(n).

2. Mikroemulsion nach Anspruch 1, worin das durchschnittliche Molekulargewicht der Fluorpolyoxyalkylene zwischen 300 und 4000 liegt.

3. Mikroemulsion nach Anspruch 1, worin das durchschnittliche Molekulargewicht der Fluorpolyoxyalkylene zwischen 400 und 1500 liegt.

4. Mikroemulsion nach einem der Ansprüche 2 bis 3, worin die Fluorpolyoxyalkylene aus den folgenden Klassen ausgewählt sind:

(a)

$$T_1\text{-}O(CF_2\text{-}CFO)_a(CFXO)_b\text{-}T_2$$
$$\Big|$$
$$CF_3$$

worin:
T_1 und T_2, die gleich oder voneinander verschieden sind, hydrierte Gruppen $-CF_2H$, $-CFH-CF_3$ oder perfluorierte Gruppen $-CF_3$, $-C_2F_5$, $-C_3F_7$ sind, wobei mindestens eine der Endgruppen hydriert ist, X -F oder $-CF_3$ ist, a, b Zahlen sind, so daß das Molekulargewicht im vorstehend angegebenen Bereich liegt, a/b zwischen 5 und 15 liegt;
(b)

$$T_3\text{-}O(CF_2CF_2O)_c(CF_2O)_d\text{-}T_4$$

worin:
T_3 und T_4, die gleich oder voneinander verschieden sind, hydrierte Gruppen $-CF_2H$ oder $-CF_2-CF_2H$, oder perfluorierte Gruppen $-CF_3$, $-C_2F_5$ sind, wobei mindestens eine der Endgruppen hydriert ist, c, d Zahlen sind, so daß das Molekulargewicht in dem vorstehend angegebenen Bereich liegt, c/d zwischen 0,3 und 5 liegt;
(c)

$$T_5\text{-}O\text{-}(CF_2\text{-}CFO)_e(CF_2CF_2O)_f(CFXO)_g\text{-}T_6$$
$$\Big|$$
$$CF_3$$

worin:
T_5 und T_6, die gleich oder voneinander verschieden sind, hydrierte Gruppen $-CF_2H$, $-CF_2CF_2H$ oder $-CFH-CF_3$ oder perfluorierte Gruppen $-CF_3$, $-C_2F_5$, $-C_3F_7$ sind, wobei mindestens eine der Endgruppen hydriert ist, X -F oder $-CF_3$ bedeutet, e, f, g Zahlen sind, so daß das Molekulargewicht in dem vorstehend angegebenen Bereich liegt, e/(f+g) zwischen 1 und 10 liegt, f/g zwischen 1 und 10 liegt;
(d)

$$T_7-O(CF_2-\underset{\substack{|\\ CF_3}}{C}FO)_h-T_8$$

worin:
T_7 und T_8 hydrierte Gruppen $-CFH-CF_3$ oder perfluorierte Gruppen $-C_2F_5$, $-C_3F_7$ sind, wobei mindestens eine der Endgruppen hydriert ist, h eine Zahl ist, so daß das Molekulargewicht im vorstehend angegebenen Bereich liegt:
(e)

$$T_9-O(CZ_2CF_2CF_2O)_i-T_{10}$$

worin:
Z F oder H bedeutet, T_9 und T_{10}, die gleich oder voneinander verschieden sind, hydrierte Gruppen $-CF_2H$ oder $-CF_2CF_2H$ oder perfluorierte Gruppen $-CF_3$, $-C_2F_5$, $-C_3F_7$ sind, wobei mindestens eine der Endgruppen hydriert ist, i eine Zahl ist, so daß das Molekulargewicht im vorstehend angegebenen Bereich liegt,
(f)

$$T_{11}-O(CF_2O)_j(CF_2\underset{\substack{|\\ OR_f}}{C}FO)_k(\underset{\substack{|\\ OR_f}}{C}FO)_l-T_{12}$$

worin:
R_f $-CF_3$, $-C_2F_5$ oder $-C_3F_7$ ist, T_{11} und T_{12}, die gleich oder voneinander verschieden sind, hydrierte Gruppen $-CF_2H$, $-CF_2CF_2H$, $-CFH-OR_f$ oder perfluorierte Gruppen $-CF_3$, $-C_2F_5$, $-C_3F_7$ sind, wobei mindestens eine der Endgruppen hydriert ist, j, k, 1 Zahlen sind, so daß das Molekulargewicht im vorstehend angegebenen Bereich liegt, k+1 und j+k+1 mindestens gleich 2 sind, k/(j+l) zwischen 10^{-2} und 10^3 liegt, 1/j zwischen 10^{-2} und 10^2 liegt;
(g)

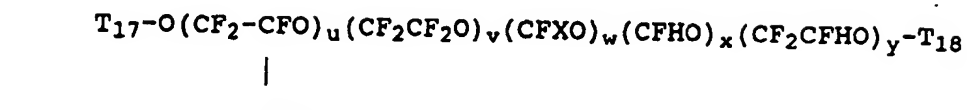
$$T_{13}-O(CF_2-\underset{\substack{|\\ CF_3}}{C}FO)_m(CFXO)_n(CFHO)_o(CF_2CFHO)_p-T_{14}$$

worin:
T_{13} und T_{14}, die gleich oder voneinander verschieden sind, hydrierte Gruppen $-CF_2H$, $-CFH-CF_3$ oder perfluorierte Gruppen $-CF_3$, $-C_2F_5$, $-C_3F_7$ sind, wobei mindestens eine der Endgruppen hydriert ist, X -F oder $-CF_3$ bedeutet, m, n, o, p Zahlen sind, so daß das Molekulargewicht im vorstehend angegebenen Bereich liegt, m/n zwischen 5 und 40 liegt, m/(o+p) zwischen 2 und 50 liegt, o+p mindestens 3 beträgt, o niedriger als p ist;
(h)

$$T_{15}-O(CF_2CF_2O)_q(CF_2O)r(CFHO)_s(CF_2CFHO)_t-T_{16}$$

worin:
T_{15} und T_{16}, die gleich oder voneinander verschieden sind, hydrierte Gruppen $-CF_2H$, $-CF_2-CF_2H$ oder perfluorierte Gruppen $-CF_3$, $-C_2F_5$ sind, wobei mindestens eine der Endgruppen hydriert ist, q, r, s, t Zahlen sind, so daß das Molekulargewicht im vorstehend angegebenen Bereich liegt, q/r zwischen 0,5 und 2 liegt, (q+r)/

(s+t) zwischen 3 und 40 liegt, s+t mindestens 3 ist, s kleiner als t ist;
(i)



worin:
T_{17} und T_{18}, die gleich oder voneinander verschieden sind, hydrierte Gruppen $-CF_2H$, $-CF_2CF_2H$, $-CFH-CF_3$ oder perfluorierte Gruppen $-CF_3$, $-C_2F_5$, $-C_3F_7$ sind, wobei mindestens eine der Endgruppen hydriert ist, X -F oder $-CF_3$ ist, u, v, w, x, y Zahlen sind, so daß das Molekulargewicht im vorstehend angegebenen Bereich liegt, (u+v)/w zwischen 5 und 40 liegt, (u+v)/(x+y) zwischen 2 und 50 liegt, x+y mindestens 3 ist, x kleiner als y ist.

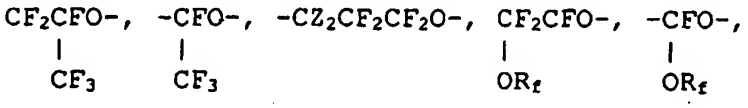
5. Mikroemulsion nach einem der vorstehenden Ansprüche, umfassend weiterhin ein begleitendes grenzflächenaktives Mittel.

6. Mikroemulsion nach Anspruch 5, worin das begleitende grenzflächenaktive Mittel aus hydrierten oder fluorierten C_1-C_6-Alkoholen ausgewählt ist.

Revendications

1. Micro-émulsion du type huile dans l'eau ou eau dans l'huile, formée au niveau macroscopique d'une phase liquide unique ayant un aspect limpide ou opalescent, stable dans une certaine plage de température, comprenant :

(a) une solution aqueuse
(b) un fluoropolyoxyalkylène constitué par des motifs répétitifs, distribués de façon statistique le long de la chaîne, choisis parmi : -CFZO, -CF2CFZO-,



où Z est H ou F, R_f est $-CF_3$, $-C_2F_5$, ou $-C_3F_7$; et par des groupes terminaux hydrogénés choisis parmi $-CF_2H$, $-CF_2CF_2H$, $-CFH-CF_3$, et $-CFH-OR_f$, où R_f est tel que défini ci-dessus, ou des groupes terminaux perfluorés choisis parmi $-CF_3$, $-C_2F_5$ et $-C_3F_7$, au moins l'un des groupes terminaux étant hydrogéné ;
(c) un tensioactif fluoré choisi parmi les classes suivantes : les acides perfluorocarboxyliques ou perfluorosulfoniques en C_5 à C_{11} et leurs sels ; les acides monocarboxyliques ou dicarboxyliques dérivant de perfluoropolyoxyalkylènes et leurs sels ; les tensioactifs non-ioniques formés par une chaîne perfluoropolyoxyalkylène liée à une chaîne polyoxyalkylène, les tensioactifs cationiques ayant une ou plusieurs chaînes perfluoroalkyle et/ou perfluorooxyalkylène.

2. Micro-émulsion selon la revendication 1, dans laquelle la masse moléculaire moyenne des fluoropolyoxyalkylènes est comprise entre 300 et 4000.

3. Micro-émulsion selon la revendication 1, dans laquelle la masse moléculaire moyenne des fluoropolyoxyalkylènes est comprise entre 400 et 1500.

4. Micro-émulsion selon l'une quelconque des revendications 2 et 3, dans laquelle les fluoropolyoxyalkylènes sont choisis parmi les classes suivantes :

(a)

$$T_1\text{-}O(CF_2\text{-}\underset{\displaystyle CF_3}{CF}O)_a(CFXO)_b\text{-}T_2$$

où :

T_1 et T_2, identiques ou différents, sont des groupes hydrogénés $-CF_2H$, $-CFH-CF_3$, ou des groupes perfluorés $-CF_3$, $-C_2F_5$, $-C_3F_7$, au moins l'un des groupes terminaux étant hydrogéné ; X est -F ou $-CF_3$; a et b sont des nombres tels que la masse moléculaire soit comprise dans la plage indiquée cidessus, a/b est comprise entre 5 et 15 ;

(b)

$$T_3\text{-}O(CF_2CF_2O)_c(CF_2O)_d\text{-}T_4$$

où :

T_3 et T_4, identiques ou différents, sont des groupes hydrogénés $-CF_2H$ ou $-CFH-CF_3$, ou des groupes perfluorés $-CF_3$, $-C_2F_5$, au moins l'un des groupes terminaux étant hydrogéné ; c, d sont des nombres tels que la masse moléculaire soit comprise dans la plage indiquée ci-dessus, c/d est comprise entre 0,3 et 5 ;

(c)

$$T_5\text{-}O(CF_2\text{-}\underset{\displaystyle CF_3}{CF}O)_e(CF_2CF_2O)_f(CFXO)_g\text{-}T_6$$

où :

T_5 et T_6, identiques ou différents, sont des groupes hydrogénés $-CF_2H$, $-CF_2CF_2H$, ou $-CFH-CF_3$, ou des groupes perfluorés $-CF_3$, $-C_2F_5$, $-C_3F_7$, au moins l'un des groupes terminaux étant hydrogéné ; X est -F ou $-CF_3$; e, f et g sont des nombres tels que la masse moléculaire soit comprise dans la plage indiquée ci-dessus, e/(f+g) est comprise entre 1 et 10 ;

(d)

$$T_7\text{-}O(CF_2\text{-}\underset{\displaystyle CF_3}{CF}O)_h\text{-}T_2$$

où :

T_7 et T_8 sont des groupes hydrogénés $-CFH-CF_3$, ou des groupes perfluorés $-C_2F_6$, $-C_3F_7$, au moins l'un des groupes terminaux étant hydrogéné ; h est un nombre tel que la masse moléculaire soit comprise dans la plage indiquée ci-dessus ;

(e)

$$T_9\text{-}O(CZ_2CF_2CF_2O)_i\text{-}T_{10}$$

où :

Z est F ou H ; T_9 et T_{10}, identiques ou différents, sont des groupes hydrogénés $-CF_2H$ ou $-CF_2-CF_2H$, ou des groupes perfluorés $-CF_3$, $-C_2F_5$, $-C_3F_7$, au moins l'un des groupes terminaux étant hydrogéné ; i est un nombre tel que la masse moléculaire soit comprise dans la plage indiquée ci-dessus ;

(f)

$$T_{11}-O(CF_2O)_j(CF_2CFO)_k(CFO)_l-T_{12}$$
$$\qquad\qquad\qquad\quad |\qquad\quad |$$
$$\qquad\qquad\qquad OR_f \quad OR_f$$

où :
R_f est $-CF_3$, $-C_2F_5$, ou $-C_3F_7$; T_{11} et T_{12}, identiques ou différents, sont des groupes hydrogénés $-CF_2H$, $-CF_2CF_2H$, $-CFH-OR_f$, ou des groupes perfluorés $-CF_3$, $-C_2F_5$, $-C_3F_7$, au moins l'un des groupes terminaux étant hydrogéné ; j, k, 1 sont des nombres tels que la masse moléculaire soit comprise dans la plage indiquée ci-dessus, k+1 et j+k+l sont au moins égales à 2, k/(j+l) est comprise entre 10^{-2} et 10^3, 1/j est comprise entre 10^{-2} et 10^2 ;
(g)

$$T_{13}-O(CF_2-CFO)_m(CFXO)_n(CFHO)_o(CF_2CFHO)_p-T_{14}$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad CF_3$$

où :
T_{13} et T_{14}, identiques ou différents, sont des groupes hydrogénés $-CF_2H$, $-CFH-CF_3$, ou des groupes perfluorés $-CF_3$, $-C_2F_5$, $-C_3F_7$, au moins l'un des groupes terminaux étant hydrogéné ; X est -F ou $-CF_3$; m, n, o, p sont des nombres tels que la masse moléculaire soit comprise dans la plage indiquée ci-dessus, m/n est comprise entre 5 et 40, m/(o+p) est comprise entre 2 et 50, o+p vaut au moins 3, o est inférieur à p ;
(h)

$$T_{15}-O(CF_2CF_2O)_q(CF_2O)_r(CFHO)_s(CF_2CFHO)_t-T_{16}$$

où :
T_{15} et T_{16}, identiques ou différents, sont des groupes hydrogénés $-CF_2H$, $-CFH-CF_3$, ou des groupes perfluorés $-CF_3$, $-C_2F_5$, au moins l'un des groupes terminaux étant hydrogéné q, r, s, t sont des nombres tels que la masse moléculaire soit comprise dans la plage indiquée ci-dessus, q/r est comprise entre 0,5 et 2, (q+r)/(s+t) est comprise entre 3 et 40, s+t vaut au moins 3, s est inférieur à t ;
(i)

$$T_{17}-O(CF_2-CFO)_u(CF_2CF_2O)_v(CFXO)_w(CFHO)_x(CF_2CFHO)_y-T_{18}$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad CF_3$$

où :
T_{17} et T_{18}, identiques ou différents, sont des groupes hydrogénés $-CF_2H$, $-CF_2CF_2H$ $-CFH-CF_3$, ou des groupes perfluorés $-CF_3$, $-C_2F_5$, $-C_3F_7$, au moins l'un des groupes terminaux étant hydrogéné ; X est -F ou $-CF_3$; u, v, w, x, y sont des nombres tels que la masse moléculaire soit comprise dans la plage indiquée ci-dessus, (u+v)/w est comprise entre 5 et 40, (u+v)/(x+y) est comprise entre 2 et 50, x+y vaut au moins 3, x est inférieur à y.

5. Micro-émulsion selon l'une quelconque des revendications précédentes, comprenant en outre un cotensioactif.

6. Micro-émulsion selon la revendication 5, dans laquelle le cotensioactif est choisi parmi les alcools en C_1 à C_6 hydrogénés ou fluorés.